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Dielectric and piezoelectric properties of [0 0 1] and [0 1 1]-poled relaxor ferroelectric PZN–PT and PMN–PT single crystals

K.K. Rajan [a,*], M. Shanthi [a], W.S. Chang [a], J. Jin [b], L.C. Lim [a,b]

[a] National University of Singapore, Department of Mechanical Engineering, 10 Kent Ridge Crescent, Singapore 119260, Singapore
[b] Microfine Materials Technologies Pte Ltd., 10 Bukit Batok Crescent, #06-02 The Spire, Singapore 658079, Singapore

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Abstract

The properties of PZN–PT and PMN–PT single crystals of varying compositions and orientations have been investigated. Among the various compositions studied, [0 0 1]-optimally poled PZN-(6–7)%PT and PMN-30%PT exhibit superior dielectric and piezoelectric properties, with $K^T \approx 6800$–8000, $d_{33} \approx 2800$ pC/N, $d_{31} \approx -(1200$–$1800)$ pC/N for PZN-(6–7)%PT; and $K^T = 7500$–9000, $d_{33} = 2200$–2500 pC/N and $d_{31} = -(1100$–$1400)$ pC/N for PMN-30%PT. These two compositions are also fairly resistant to over-poling. The [0 0 1]-poled electromechanical coupling factors (k_{33}, k_{31} and k_t) are relatively insensitive to crystal composition. [0 1 1]-optimally poled PZN-7%PT single crystal also exhibits extremely high d_{31} values of up to -4000 pC/N with $k_{31} \approx 0.90$–0.96. While [0 1 1]-poled PZN-7%PT single crystal becomes over-poled with much degraded properties when poled at and above 0.6 kV/mm, PZN-6%PT crystal shows no signs of over-poling even when poled to 2.0 kV/mm. The presence of a certain amount (i.e., 10–15%) of orthorhombic phase in a rhombohedral matrix has been found to be responsible for the superior transverse piezoelectric properties of [0 1 1]-optimally poled PZN-(6–7)%PT. The present work shows that flux-grown PZN–PT crystals exhibit superior and consistent properties and improved over-poling resistance to flux-grown PMN–PT crystals and that, for or a given crystal composition, flux-grown PMN–PT crystals exhibit superior over-poling resistance to their melt-grown counterparts.

Keywords: Relaxor-ferroelectrics; Single crystal; Dielectric constant; Piezoelectric properties; Poling

1. Introduction

Relaxor-based ferroelectric single crystals of $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZN–PT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) exhibit exceptional dielectric and electromechanical properties compared to state-of-the-art lead zirconate titanate (PZT) ceramics [1,2] and have generated much interest among contemporary scientists and engineers in the field. These single crystals are potential new-generation piezo materials for high-performance piezo devices and systems including ultrasound medical imaging probes, sonars for underwater communications, sensors/actuators, etc.

PZN and PMN single crystals with a rhombohedral symmetry form solid solutions with normal ferroelectric lead titanate (PT) of tetragonal symmetry, with their morphotropic phase boundaries (MPBs) located at 9–11 and 33–35%PT, respectively. Although the growth of PZN–PT and PMN–PT single crystals and their characterization were performed more than a decade ago [3], not much interest had been generated until the works of Park and coworkers [1,2] were published. They reported extremely high property values ($k_{33} > 0.90$, $d_{33} > 1500$ pC/N, $K^T > 5000$) for [0 0 1]-poled crystals of compositions close to the MPBs, even though the polar axis is along one of the $[1\,1\,1]_c$ directions. Since then, many works have been published on the properties of [0 0 1]-poled PZN–PT and PMN–PT single crystals. The exceptional behaviour of these single crystals has been believed to be a result of the mixed ferroelectric rhombohedral and tetragonal phases present. However, high energy X-ray revealed by surprise an intermediate monoclinic/orthorhombic phase within a narrow compositional range lying between the rhombohedral and tetragonal phases [4–6]. More recently, Singh and Pandey [7] and Bertram et al. [8] have performed detailed rietveld analysis on various compositions of PMN–PT and PZN–PT, respectively, and identified the

* Corresponding author. Tel.: +65 91867487; fax: +65 68748103.
E-mail address: kkrajan@nus.edu.sg (K.K. Rajan).

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types and amounts of phases present in the materials. This paper attempts to study the properties of both [0 0 1]- and [0 1 1]-poled flux-grown PZN–PT and PMN–PT single crystals. The poling responses of PZN–PT and PMN–PT single crystals of different compositions and orientation have been investigated and evidence for possible induced metastable phases are presented and discussed. Attempts are also made to compare the properties of flux- and melt-grown PMN–PT single crystals.

2. Experimental details

PZN-xPT and PMN-yPT single crystals of different PT contents, namely, $x = 4.5$–8.0% and $y = 28$–32%, respectively, were supplied by Microfine Materials Technologies P/L (Singapore). They were grown by the high-temperature flux technique with PbO-based fluxes [9–11]. All grown crystals exhibited obvious (0 0 1) growth facets, indicating that under the growth conditions used, the growth of PZN–PT and PMN–PT crystals is dominated by the (0 0 1) layer growth process. As both the structures and properties of these crystals are sensitive to PT content, their compositions were determined using their Curie temperatures [9–11]. The crystals were sliced and diced into $[1\,0\,0]^L/[0\,1\,0]^W/[0\,0\,1]^T$ k_{31}- and k_t-plates and k_{33}-bars, of 7^L mm × 2^W mm × 0.5^T mm, 5^L mm × 5^W mm × 0.5^T mm and 3^L mm × 3^W mm × 9^T mm in dimensions, respectively. To check the effect of length orientation on k_{31} properties, $[1\,1\,0]^L/[1\text{–}10]^W/[0\,0\,1]^T$ k_{31}-plates were also prepared. As for [0 1 1]-poled samples, k_{31}-mode plates of 9.0^L mm × 3.0^W mm × 0.5^T mm in dimensions were diced from (0 1 1) wafers with two different length orientations, i.e., $[1\,0\,0]^L/[01\text{–}1]^W/[0\,1\,1]^T$ and $[01\text{–}1]^L/[1\,0\,0]^W/[0\,1\,1]^T$. The samples were coated with nichrome–gold/palladium electrodes on appropriate faces. To establish the optimum poling fields for both the plate and bar samples, the samples were poled progressively in silicone oil at room temperature from 0.2 to 2.0 kV/mm for the k_{31}- and k_t-plates and from 0.2 to 0.5 kV/mm for the k_{33}-bars. After each poling step, the dielectric constant (K^T, measured at 1 kHz) and electromechanical coupling factors (k_{33}, k_{31} and k_t, measured with the resonance technique) were determined using an *Agilent 4294* impedance network analyzer and the piezoelectric coefficients (d_{33} and d_{31}) were obtained with a *Berlincourt*-type meter. The poling field giving the best property values was taken as the optimum poling condition. To identify the phases present, X-ray diffraction studies were carried out. The X-ray radiations used were Cu Kα_1 (0.154056 nm) and Cu Kα_2 (0.154439 nm). The scanning rate used was 0.5° 2θ/min and pure silicon powder was used as an internal reference. In addition, polarized light microscopy and temperature dependence of dielectric constant were also performed.

3. Effects of poling on phases in PZN–PT and PMN–PT

Earlier in situ X-ray diffraction studies have revealed that poling at high fields can induce a metastable monoclinic or orthorhombic phase other than rhombohedral and tetragonal phases [4]. Using powder diffraction technique, several researchers have shown the presence of these new phases in unpoled samples [5–8]. Moreover, the amount of these new phases depends sensitively on the composition of the crystal. For instance, compositions close to the MPBs are more prone to have these metastable phases due to their comparable energy states and the presence of transformation stresses in the material. The presence of metastable phases in unpoled and poled relaxor single crystals can also be manifested from the temperature dependence of their dielectric constant [12,13]. Although it is difficult to distinguish the new monoclinic phase from a stressed rhombohedral state due to their close lattice and structural coherence, one may conclude that both PZN–PT and PMN–PT systems are complicated in phase/domain structure.

We have performed X-ray diffraction (XRD) study and polarized light microscopy with poled plates of PZN–PT and PMN–PT single crystals of different compositions. Our results have revealed that for crystal compositions away from the MPBs, i.e., PZN-4.5%PT and PMN-28%PT, the poled structures are largely rhombohedral. This holds for both [0 0 1]- and [0 1 1]-poled crystals. In contrast, for PZN–PT and PMN–PT single crystals of compositions near the MPBs, the resultant domain structures/phases depend sensitively on the poling field strength used. They remain largely rhombohedral at low poling fields but with increased amounts of metastable phases upon being poled at high fields. Fig. 1 compares the (0 0 2) X-ray profiles of [0 0 1]-poled PMN-28%PT and PMN-32%PT samples. In this figure, the XRD profiles have been corrected for instrumental broadening and that due to Cu Kα_2 radiation using built-in software. This figure shows that the (0 0 2) XRD profile of PMN-28%PT single crystal plate, which is compositionally away from the MPB, gives a predominantly rhombohedral peak at $2\theta \approx 45.10°$. Note, however, that the rhombohedral peak is asymmetrical and broad, suggesting the presence of minute amounts of metastable phases and/or the rhombohedral phase being highly stressed. On the other hand, the (0 0 2) XRD profile of the over-poled PMN-32%PT plate reveals a prominent shoulder at $2\theta \approx 44.80°$ in addition to the $(0\,0\,2)_R$ peak at $2\theta \approx 45.10°$.

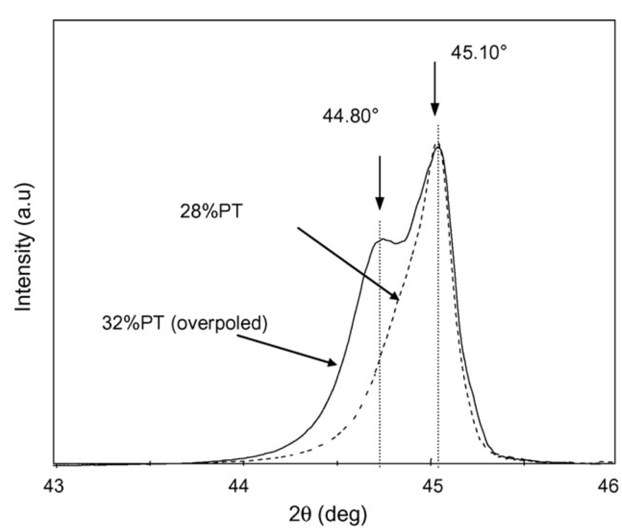

Fig. 1. (0 0 2) X-ray diffraction peaks of [0 0 1]-poled PMN–PT single crystals: dashed curve — PMN-28%PT; solid curve — PMN-32%PT in over-poled state.